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THE MELTING POINT EXPERIMENT

A **melting point** is the temperature at which the first crystal just starts to melt until the temperature at which the last crystal just disappears. Thus the melting point (abbreviated M.P.) is actually a **melting range**. You should report it as such, even though it is *called* a melting point, for example, M.P. 147–149°C.

People always read the phrase as *melting point* and never as *melting point*. There is this uncontrollable, driving urge to report one number. No matter how much I've screamed and shouted at people *not* to report one number, they almost always do. It's probably because handbooks list only one number, the upper limit.

Generally, melting points are taken for two reasons.

1. **Determination of purity.** If you take a melting point of your compound and it starts melting at 60°C and doesn't finish until 180°C, you might suspect something is wrong. A melting range *greater than* 2°C usually indicates an impure compound. (As with all rules, there are exceptions. There aren't many to this one, though.)
2. **Identification of unknowns.**
 - a. If you have an unknown solid, take a melting point. Many books (ask your instructor) contain tables of melting points and lists of compounds that may have a particular melting point. One of them may be your unknown. You may have 123 compounds to choose from. A little difficult, but that's not all the compounds in the world. Who knows?? Give it a try. If nothing else, you know the melting point.
 - b. Take your unknown and mix it *thoroughly* with some chemical you think might be your unknown. You might not get a sample of it, but you can ask. Shows you know something. Then:
 - (1) If the mixture melts at a *lower* temperature, over a *broad range*, your unknown is not the same compound.
 - (2) If the mixture melts at the *same temperature*, *same range*, it's a good bet it's the *same compound*. Try another one, though, with a different ratio of your unknown and this compound just to be sure. A *lower* melting point with a *sharp range* would be a special point called a **eutectic mixture**, and you, with all the other troubles in lab, just might accidentally hit it. On lab quizzes, this is called

"Taking a mixed melting point."

Actually, “taking a mixture melting point,” the melting point of a mixture, is more correct. But I have seen this expressed both ways.

SAMPLE PREPARATION

You usually take melting points in thin, closed end tubes called **capillary tubes**. They are also called **melting point tubes** or even **melting point capillaries**. The terms are interchangeable, and I’ll use all three.

Sometimes you may get a supply of tubes that are open on *both ends*! You don’t just use these as is. Light a burner and before you start, close off one end. Otherwise your sample will fall out of the tube (see “Closing Off Melting Point Tubes” later in this chapter).

Take melting points on *dry, solid* substances only, *never* on liquids or solutions of solids *in* liquids or on wet or even damp solids. Only on dry solids!

To help dry damp solids, place the damp solid on a piece of filter paper and fold the paper around the solid. Press. Repeat until the paper doesn’t get wet. Yes, you may have to use fresh pieces of paper. Try not to get filter paper fibers in the sample, OK?

Occasionally, you may be tempted to dry solid samples in an oven. *Don’t*—unless you are specifically instructed to. I know some students who have decomposed their products in ovens and under heat lamps. With the time they save quickly decomposing their product, they can repeat the entire experiment.

Loading the Melting Point Tube

Place a small amount of *dry* solid on a new filter paper (Fig. 46). Thrust the open end of the capillary tube into the middle of the pile of material. Some solid should be trapped in the tube. Turn the tube over, closed end down. Remove any solid sticking to the outside. The solid must now be packed down.

Traditionally, the capillary tube, turned upright with the *open end up*, is stroked with a file, or tapped on the benchtop. Unless done *carefully*, these operations *may break the tube*. A safer method is to drop the tube *closed end down*, through a length of glass tubing. You can even use your condenser or distilling column for this purpose. When the capillary strikes the benchtop, the compound will be forced into the closed end. You may have to do this several times. If there is not enough material in the M.P. tube,

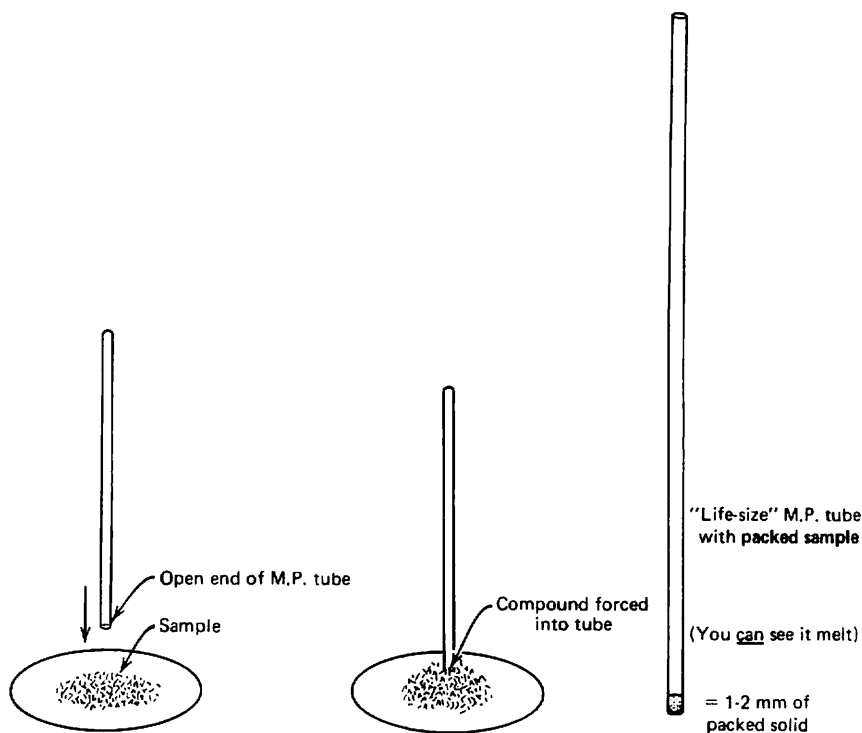


Fig. 46 Loading a Melting point tube.

thrust the open end of the tube into the mound of material and pack it down again. Use your own judgment; consult your instructor.

Use the smallest amount of material that can be seen to melt.

Closing Off Melting Point Tubes

If you have melting point tubes that are open at both ends and you try to take a melting point with one, it should come as no surprise when your compound falls out of the tube. You'll have to *close off one end* to keep your sample from falling out (Fig. 47). So light a burner and get a "stiff" small blue flame. Slowly touch the end of the tube to the side of the flame, and hold it there. You should get a yellow sodium flame, and the tube will close up. There is no need to rotate the tube. And remember, *touch—just touch*—the

edge of the flame, and hold the tube there. Don't feel you have to push the tube way into the flame.

MELTING POINT HINTS

1. Use only the smallest amount that you can see melt. Larger samples will heat unevenly.
2. Pack down the material as much as you can. Left loose, the stuff will heat unevenly.
3. Never remelt any sample. They may undergo nasty chemical changes such as oxidation, rearrangement, and decomposition.
4. Make up more than one sample. One is easy, two is easier. If something goes wrong with one, you have another. Duplicate, even triplicate runs are common.

THE MEL-TEMP APPARATUS

The Mel-Temp apparatus (Fig. 48) substitutes for the Thiele tube or open beaker and hot oil methods (see "Using the Thiele Tube" later in this chapter). Before you use the apparatus, there are a few things you should look for.

1. **Line cord.** Brings AC power to the unit. Should be plugged into a live wall socket. [See J. E. Leonard and L. E. Mohrmann, *J. Chem. Educ.*, **57**, 119 (1980), for a modification in the wiring of older units, to make them less lethal. It seems that even with the three-prong plug, there can still be a shock hazard. *Make sure your instructor knows about this!*]
2. **On-off switch.** Turns the unit on or off.

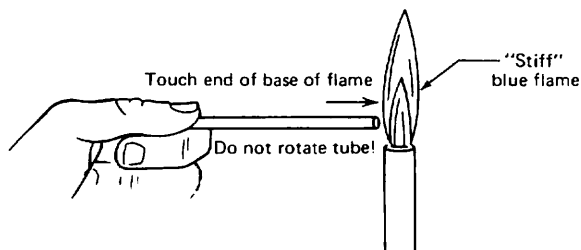


Fig. 47 Closing off a M.P. tube with a flame.

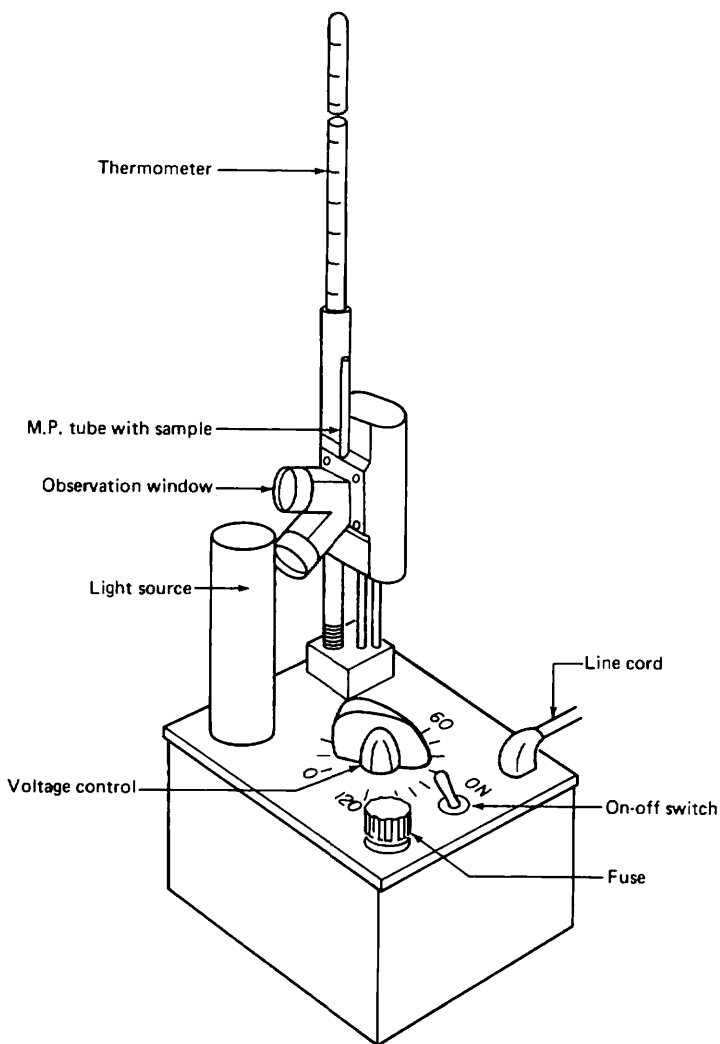


Fig. 48 The Mel-Temp apparatus.

3. **Fuse.** Provides electrical protection for the unit.
4. **Voltage control.** Controls the *rate* of heating, *not the temperature!* The higher the setting, the faster the temperature rise.
5. **Light source.** Provides illumination for samples.
6. **Eyepiece.** Magnifies the sample (Fig. 49).
7. **Thermometer.** Gives the temperature of the sample, and upsets the digestion when you're not careful and you snap it off in the holder.

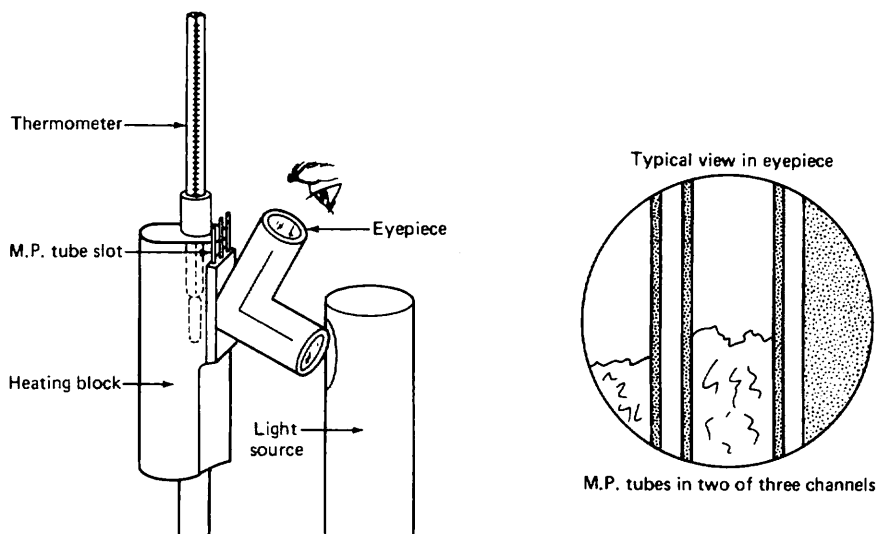


Fig. 49 Close-up of the viewing system.

OPERATION OF THE MEL-TEMP APPARATUS

1. *Imagine yourself getting burned if you're not careful.* Never assume the unit is cold.
2. Place loaded M.P. tube in one of the three channels in the opening at the top of the unit (Fig. 49).
3. Set the voltage control to zero if necessary. There are discourteous folk who do not reset the control when they finish using the equipment.
4. Turn the on-off switch to ON. The light source should illuminate the sample. If not, call for help.
5. Now science turns into art. Set the *voltage control* to *any* convenient setting. The point is to get up to *within 20°C* of the *supposed* melting point. Yep, that's right. If you have no idea what the melting point is, it may require several runs as you keep skipping past the points with a temperature rise of 5-10°C per minute. A convenient setting is 40. This is just a suggestion, not an article of faith.
6. After you've melted a sample, *throw it away!*
7. Once you have an idea of the melting point (or looked it up in a handbook, or were told), *get a fresh sample*, and bring the temperature up quickly at about 5-10°C per minute to *within 20°C* of this approximate melting point. Then turn down the *voltage control* to get a 2°C per minute rise. Patience!

8. When the first crystals *just start to melt*, record the temperature. When the *last crystal just disappears*, record the temperature. If both points appear to be the same, either the sample is extremely pure or the temperature rise was *too fast*.
9. Turn the on-off switch to OFF. You can set the voltage control to zero for the next person.
10. Remove all capillary tubes.

Never use a wet rag or sponge to quickly cool off the heating block. This might permanently warp the block. You can use a cold metal block to cool it if you're in a hurry. Careful. If you slip, you may burn yourself.

THE FISHER-JOHNS APPARATUS

The Fisher-Johns apparatus (Fig. 50) is different in that you don't use capillary tubes to hold the sample. Instead, you sandwich your sample between two round microscope cover slides (thin windows of glass) on a heating block. This type of melting point apparatus is called a **hot stage**. It comes complete with spotlight. Look for the following.

1. **Line cord** (at the back). Brings AC power to the unit. Should be plugged into a live wall socket.
2. **On-off switch**. Turns the unit on or off.
3. **Fuse** (also at the back). Provides electrical protection for the unit.
4. **Voltage control**. Controls the *rate* of heating, *not the temperature!* The higher the setting, the faster the temperature rise.
5. **Stage light**. Provides illumination for samples.

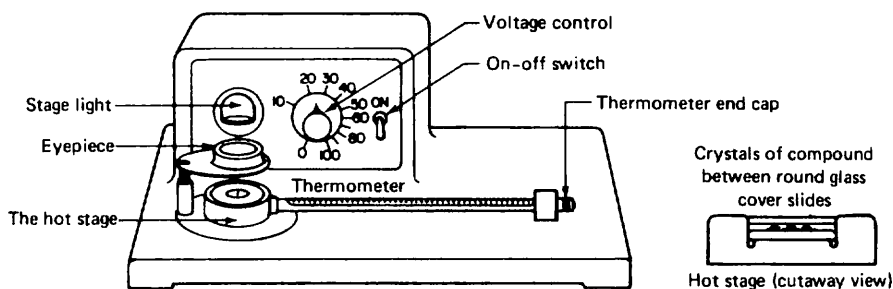


Fig. 50 The Fisher-Johns Apparatus.

6. ***Eyepiece.*** Magnifies the sample.
7. ***Thermometer.*** Gives the temperature of sample.
8. ***Thermometer end cap.*** Keeps the thermometer from falling out. If the cap becomes loose, the thermometer tends to go belly-up and the markings turn over. Don't try to fix this while the unit is hot. Let it cool so you won't get burned.
9. ***The hot stage.*** This is the heating block that samples are melted on.

OPERATION OF THE FISHER-JOHNS APPARATUS

1. *Don't assume that the unit is cold.* That is a good way to get burned.
2. Keep your grubby fingers off the cover slides. Use tweezers or forceps.
3. Place a clean round glass cover slide in the well on the hot stage. *Never melt any samples directly on the metal stage.* Ever!
4. Put a few crystals on the glass. Not too many. As long as you can see them melt, you're all right.
5. Put another cover slide on top of the crystals to make a sandwich.
6. Set the voltage control to zero if it's not already there.
7. Turn on-off switch to ON. The light source should illuminate the sample. If not, call for help!
8. Now science turns into art. Set the *voltage control* to any convenient setting. The point is to get up to *within 20°C* of the *supposed* melting point. Yep, that's right. If you have no idea what the melting point is, it may require several runs as you keep skipping past the point with a temperature rise of 5-10°C per minute. A convenient setting is 40. This is just a suggestion, not an article of faith.
9. After you've melted a sample, let it cool, and remove the sandwich of sample and cover slides. *Throw it away!* Use an appropriate waste container.
10. Once you have an idea of the melting point (or have looked it up in a handbook, or you were told), *get a fresh sample*, and bring the temperature up quickly at about 5-10°C per minute to *within 20°C* of this approximate melting point. Then turn down the *voltage control* to get a *2°C per minute rise*. Patience!
11. When the first crystals *just start to melt*, record the temperature. When the last crystal *just disappears*, record the temperature. If both points appear to be the same, either the sample is extremely pure or the temperature rise was *too fast*.

12. Turn the on-off switch to OFF. Now set the voltage control to zero.
13. Let the stage cool, then remove the sandwich.

THE THOMAS-HOOVER APPARATUS

The Thomas-Hoover apparatus (Fig. 51) is the electromechanical equivalent of the Thiele tube or open beaker and hot oil methods (see "Using the Thiele Tube" later in this chapter). It has lots of features, and you should look for the following.

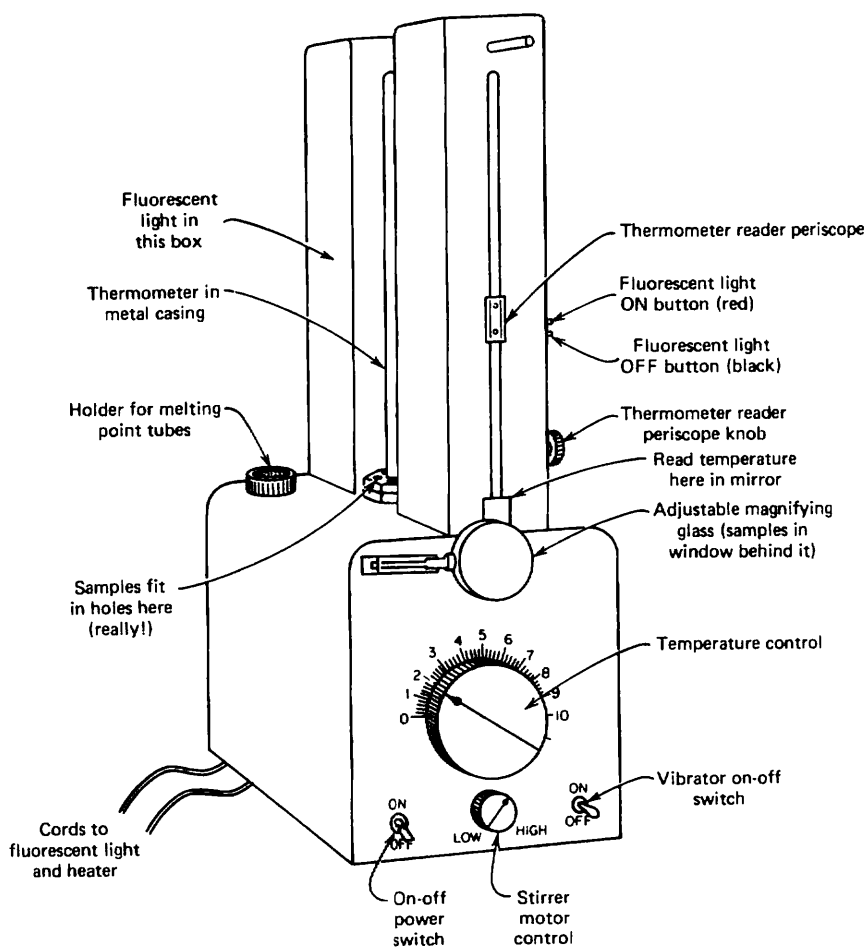


Fig. 51 The Thomas-Hoover Apparatus.

1. **Light box.** At the top of the device, toward the back, a box holds a fluorescent light bulb behind the thermometer. On the right side of this box are the fluorescent light switches.
2. **Fluorescent light switches.** Two buttons. Press and hold the red button down for a bit to light the lamp; press the black button to turn the lamp off.
3. **Thermometer.** A special 300° thermometer in a metal jacket is immersed in the oil bath that's in the lower part of the apparatus. Two slots have been cut in the jacket to let light illuminate the thermometer scale from behind and to let a thermometer periscope read the thermometer scale from the front.
4. **Thermometer periscope.** In front of the thermometer, this periscope lets you read a small magnified section of the thermometer scale. By turning the small knob at the lower right of this assembly, you track the movement of the mercury thread, and an image of the thread and temperature scale appears in a stationary mirror just above the sample viewing area.
5. **Sample viewing area.** A circular opening is cut in the front of the metal case so that you can see your samples in their capillary tubes (and the thermometer bulb) all bathed in the oil bath. You put the tubes into the oil bath through the holes in the capillary tube stage.
6. **Capillary tube stage.** In a semicircle about the bottom of the jacketed thermometer, yet behind the thermometer periscope, are five holes through which you can put your melting point capillaries.
7. **Heat.** Controls the rate of heating, not the temperature. The higher the setting, the faster the temperature rise. At Hudson Valley Community College, we've had a stop put in and you can only turn the dial as far as the number 7. When it gets up to 10, you always smoke the oil. Don't do that.
8. **Power on-off switch.** Turns the unit on or off.
9. **Stirrer control.** Sets the speed of the stirrer from low to high.
10. **Vibrator on-off switch.** Turns the vibrator on or off. It's a spring-return switch, so you must hold the switch in the ON position. Let go, and it snaps off.
11. **Line cords.** One cord brings AC power to the heater, stirrer, sample light, and vibrator. The other cord brings power to the fluorescent light behind the thermometer. Be sure both cords are plugged into live wall sockets.

OPERATION OF THE THOMAS-HOOVER APPARATUS

1. If the fluorescent light for the thermometer is not lit, press the red button at the right side of the light box and hold it down for a bit to start the lamp. The lamp should remain lit after you release the button.
2. Look in the thermometer periscope, turn the small knob at the lower right of the periscope base, and adjust the periscope to find the top of the mercury thread in the thermometer. Read the temperature. Wait for the oil bath to cool if the temperature is fewer than 20 Celsius degrees below the approximate melting point of your compound. You'll have to wait for a room temperature reading if you have no idea what the melting point is. You don't want to plunge your sample into oil that is so hot it might melt too quickly, or at an incorrect temperature.
3. Turn the voltage control to zero if it isn't there already.
4. Turn the power on-off switch to ON. The oil bath should become illuminated.
5. Insert your capillary tube in one of the capillary tube openings in the capillary tube stage. *This is not simple.* Be careful. If you snap a tube at this point, the entire unit may have to be taken apart to remove the pieces. It appears you have to angle the tube toward the center opening and angle the tube toward you (as you face the instrument) at the same time (Fig. 52). It's as if they were placed on the surface of a conical funnel.
6. Adjust the magnifying glass for the best view of your sample.
7. Turn the stirrer knob so that the mark on the knob is about halfway between the slow and fast markings on the front panel. That's just a suggestion. I don't have any compelling reasons for it.
8. Adjust the thermometer periscope to give you a good view of the top of the mercury thread in the thermometer.
9. Now science turns into art. Set the *heat control* to *any* convenient setting. The point is to get up to *within 20°C* of the *supposed* melting point. If you have no idea what the melting point is, it may require several runs as you keep skipping past the point with a temperature rise of 5–10°C per minute. A convenient setting is 4. This is just a suggestion, not an article of faith.
10. Remember, you'll have to keep adjusting the thermometer periscope to keep the top of the mercury thread centered in the image.
11. After you've melted a sample, *throw it away!*

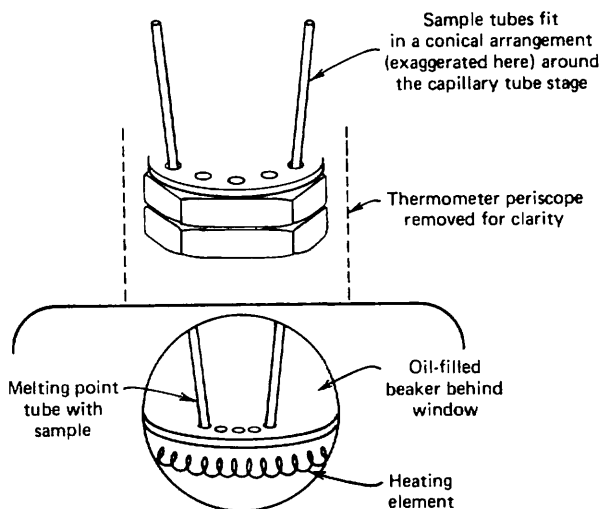


Fig. 52 Close-up of the viewing system.

12. Once you have an idea of the melting point (or looked it up in a handbook, or were told), *get a fresh sample* and bring the temperature up quickly at about $5\text{--}10^{\circ}\text{C}$ per minute to *within* 20°C of this approximate melting point. Then turn down the *heat control* to get a 2°C per minute rise. Patience!
13. When the first crystals *just start to melt*, record the temperature. When the *last crystal just disappears*, record the temperature. If both points appear to be the same, either the sample is extremely pure or the temperature rise was *too fast*. If you record the temperature with the horizontal index line in the mirror matched to the lines etched on both sides of the periscope window and the top of the mercury thread at the same time, you'll be looking at the thermometer scale head on. This will give you the smallest error in *reading* the temperature (Fig. 53).
14. Don't turn the control much past 7. You can get a bit beyond 250°C at that setting, and that should be *plenty* for any solid compound you might prepare in this lab. Above this setting, there's a real danger of smoking the oil.
15. Turn the power switch to OFF. You can also set the *heat control* to zero for the next person.
16. Press the black button on the right side of the light box and turn the fluorescent light off.
17. Remove all capillary tubes.

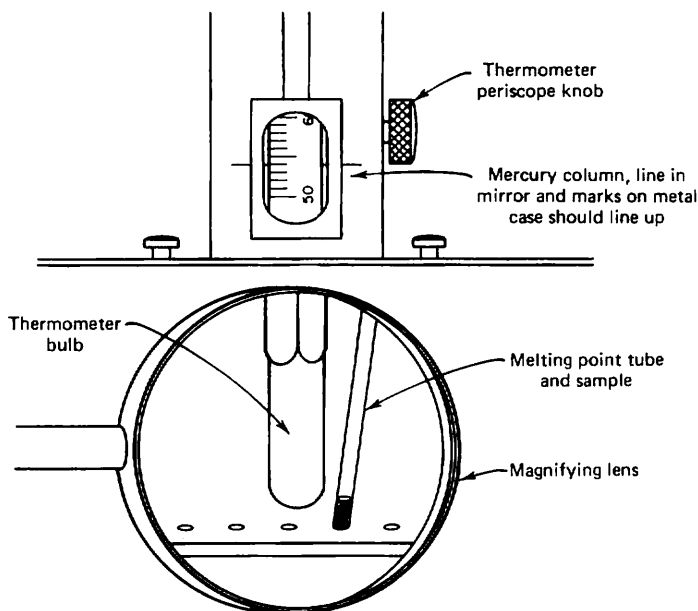


Fig. 53 Reading the temperature.

There are a few more electric melting point apparatuses around, and much of them work the same. A **sample holder**, **magnifying eyepiece**, and **voltage control** are common; an apparently essential feature of these devices is that dial markings are almost *never* temperature settings. That is, a setting of **60** will not give a temperature of 60°C but probably much higher.

USING THE THIELE TUBE

With the Thiele tube (Fig. 54), you use hot oil to transfer heat evenly to your sample in a melting point capillary, just like the metal block of the Mel-Temp apparatus does. You heat the oil in the sidearm and it expands. The hot oil goes up the sidearm, warming your sample and thermometer as it touches them. Now, the oil is cooler, and it falls to the bottom of the tube where it is heated again by a burner. This cycle goes on automatically as you do the melting point experiment in the Thiele tube.

Don't get any water in the tube or when you heat the tube the water can boil and throw hot oil out at you. Let's start from the beginning.

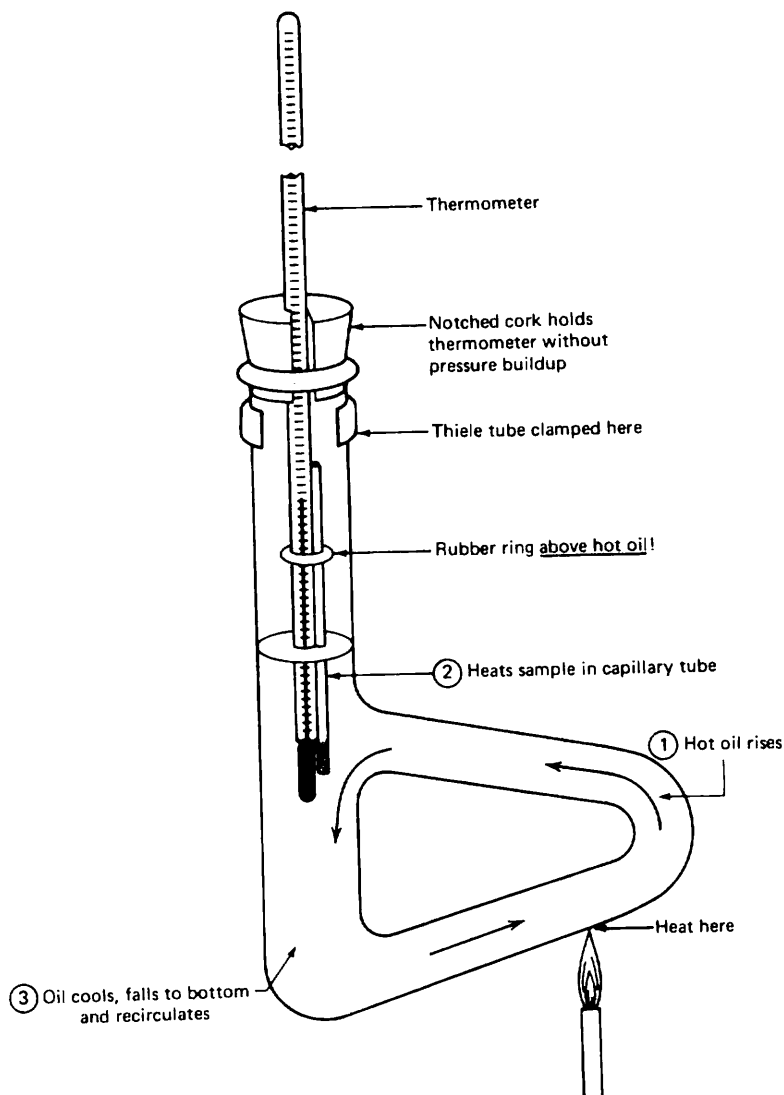


Fig. 54 Taking melting points with the Thiele tube.

Cleaning the Tube

This is a bit tricky, so don't do it unless your instructor says so. Also, check with your instructor *before* you put fresh oil in the tube.

1. Pour the old oil out into an appropriate container and let the tube drain.
2. Use a hydrocarbon solvent (hexane, ligroin, petroleum ether—and *no flames!*) to dissolve the oil that's left.
3. Get out the old soap and water and elbow grease, clean the tube, and rinse it out really well.
4. Dry the tube in a drying oven (usually $>100^{\circ}\text{C}$) thoroughly. Carefully take it out of the oven and let it cool.
5. Let your instructor examine the tube. If you get the OK, *then* add some fresh oil. Watch it. First, *no water*. Second, don't overfill the tube. Normally, the oil expands as you heat the tube. If you've overfilled the tube, oil will crawl out and get you.

Getting the Sample Ready

Here you use a loaded melting point capillary tube (see "Loading the Melting Point Tube" earlier in the chapter) and attach it directly to the thermometer. Unfortunately, the thermometer has bulges; there are some problems, and you may snap the tube while attaching it to the thermometer.

1. Get, or cut, a thin rubber ring from a piece of rubber tubing.
2. Put the *bottom* of the loaded MP tube *just above* the place where the thermometer constricts (Fig. 55), and carefully roll the rubber ring onto the MP tube.
3. Reposition the tube so that the sample is near the center of the bulb and the rubber ring is near the open end. *Make sure the tube is vertical.*

Dunking the Melting Point Tube

There are more ways of keeping the thermometer suspended in the oil than I care to list. You can cut or file a notch on the side of the cork, drill a hole, and insert the thermometer (*be careful!*). Finally, cap the Thiele tube (Fig.

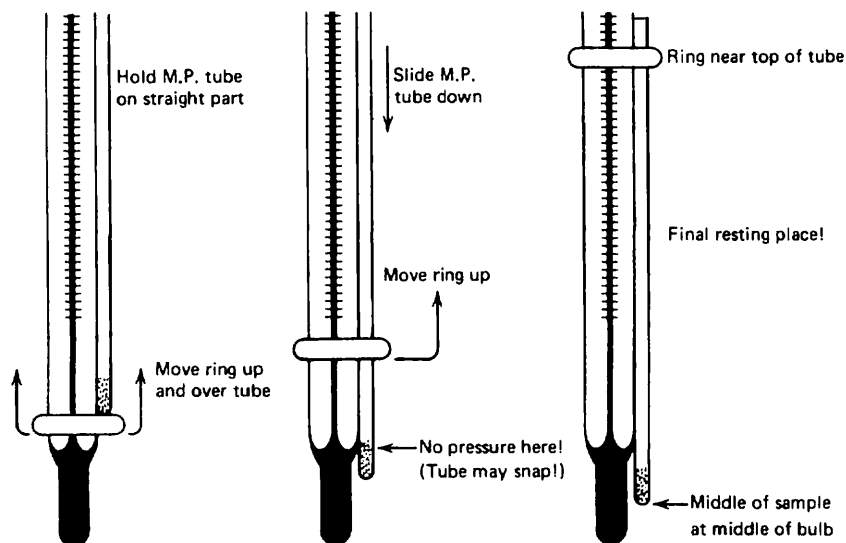


Fig. 55 Attaching M.P. tube to thermometer without a disaster.

54). The notch is there so that pressure will not build up as the tube is heated. *Keep the notch open, or the setup may explode.*

But this requires drilling or boring corks, something you try to avoid. (Why have ground-glass jointware in the undergraduate lab?) You can *gently* hold a thermometer and a cork in a clamp (Fig. 56). Not too much pressure, though!

Finally, you might put the thermometer in the **thermometer adapter** and suspend that, clamped gently by the rubber part of the adapter, and not by the ground glass end. Clamping ground glass will score the joint.

Heating the Sample

The appropriately clamped thermometer is set up in the Thiele tube as in Fig. 54. Look at this figure *now* and remember to heat the tube *carefully*—*always carefully—at the elbow. Then:*

1. If you don't know the melting point of the sample, heat the oil fairly quickly, *but no more than 10°C per minute* to get a rough melting point. And it will be rough indeed, since the temperature of the thermometer usually lags that of the sample.

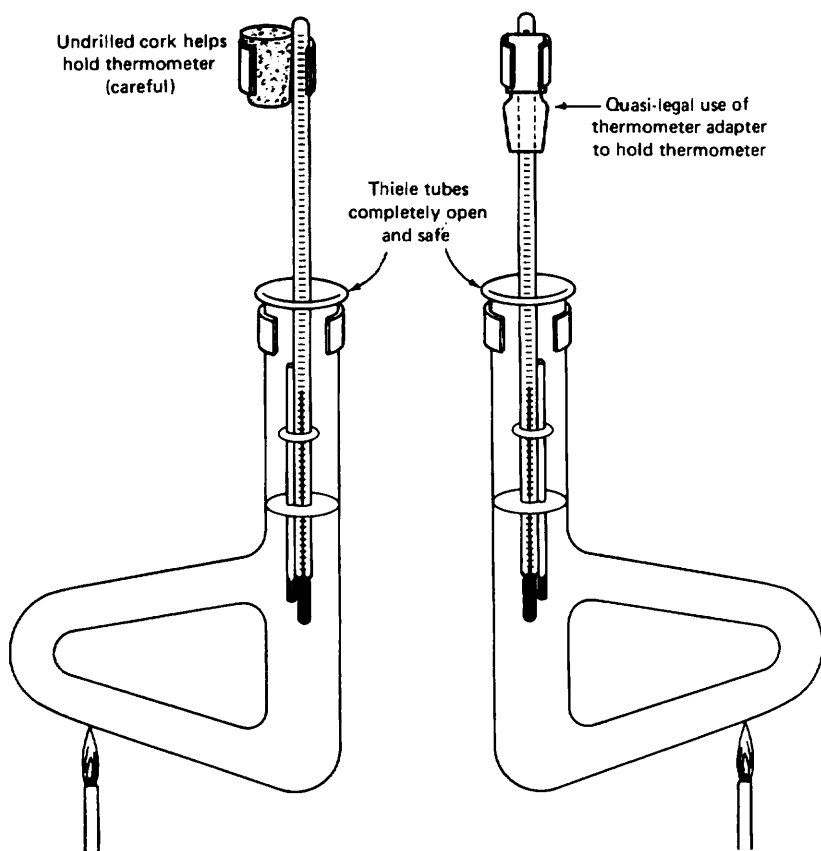


Fig. 56 Safety suspended thermometer with Thiele Tube.

2. After this sample has melted, lift the thermometer and attached sample tube *carefully (it may be HOT)* by the thermometer up at the clamp, until they are *just out of the oil*. This way the thermometer and sample can cool, and the hot oil can drain off. Wait for the thermometer to cool to about room temperature before you remove it entirely from the tube. Wipe off some of the oil, reload a melting point tube (*never remelt melted samples*), and try again. And heat at 2°C per minute this time.